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PROCESS FOR ADJUSTING THE AMOUNT OF ZINC POWDER DURING THE  
REMOVAL OF CONTAMINANTS FROM ZINC SULFATE SOLUTIONS

[VERFAHREN ZUM EINSTELLEN DER MENGE AN ZINKPULVER BEIM  
ENTFERNEN VON VERUNREINIGUNGEN AUS ZINKSULFATLOESUNGEN]

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## Patent Claims

1. A process for adjusting the amount of zinc powder utilized during the deposition of contaminants from a zinc sulfate solution provided for electrolytically refining zinc, characterized in that the amount of added zinc powder is adjusted with the aid of redox potential measurements.

2. The process of claim 1, characterized in that the amount of added zinc powder is adjusted with the aid of redox potential measurements, which are carried out during the cobalt removal stage of the solution purification.

3. The process of claim 1, characterized in that the redox potential is adjusted in such a way as zinc powder is charged for the deposition of copper that it remains within a range of -480 to -550 mV with reference to the calomel electrode.

4. The process of claim 1 and 2, characterized in that the redox potential is adjusted in such a way as zinc powder is charged for the deposition of cobalt, nickel and germanium that it remains within a range of -570 to -650 mV with reference to the calomel electrode.

5. The process of claim 1, characterized in that the amount of added zinc powder is adjusted in a batch process with the aid of redox potential measurements.

6. The process of claim 1, characterized in that the amount of added zinc powder is adjusted in a continuous process with the aid of redox potential measurements.

7. The process of claim 1, characterized in that the amount of added zinc powder is adjusted in a process that utilizes arsenic as auxiliary agent with the aid of redox potential measurements.

8. The process of claim 1, characterized in that the amount of added zinc powder is adjusted in a process that utilizes antimony as auxiliary agent with the aid of redox potential measurements.

#### Description

The invention concerns a process for removal of contaminants from zinc sulfate solutions during electrolytic refining of zinc and, in particular, for adjustment of the amount of zinc powder utilized during the removal of contaminants. The removal of contaminants, such as, for example, copper, cobalt, nickel and germanium, as well as cadmium, is carried out by cementing the latter with the aid of zinc powder, wherein the amount of zinc powder used is optimized by applying redox potential measurements.

The main raw materials used in electrolytic zinc processes are zinc concentrates, which are first roasted in

an oxidizing manner. The calcined product is dissolved in a recycled acid solution containing sulfuric acid, which is recovered from electrodeposition. The insoluble components are separated from the zinc sulfate solution produced during the dissolution process. The solution is further fed to the solution purification, wherein all of the elements nobler than zinc are removed. After the solution purification, the solution is fed to the electrolysis.

The raw solution of a zinc process contains a series of elements nobler than zinc, whose content varies according to the concentrates and other components. The most important among these are copper, cadmium, cobalt, nickel, arsenic, antimony, germanium, and thallium. Because these elements are nobler than zinc, they have a tendency to deposit on the cathode during electrolysis. This is not desired, because they contaminate the deposited zinc and because a few of these elements cause secondary reactions (hydrogen development).

Because the previously mentioned elements are nobler than zinc, they can be cemented out of the solution with the aid of metallic zinc. This process is utilized almost exclusively in zinc production, but with the exception of the process of solution purification, where the metals

nobler than zinc are removed from the zinc electrolytes with the aid of an extraction with  $\beta$ -naphthol.

Even though the cementing agent utilized during solution purification is generally zinc, a few auxiliary agents, such as, for example, arsenic or antimony, are normally also used. If antimony is utilized, the purification stages are generally continuously working stages, so that the first stage comprises the removal of cadmium and copper, and the second stage comprises the removal of cobalt and nickel; the second possible stage is therein mainly a support stage for the previous process.

There are basically two different processes that utilize arsenic as auxiliary agent for zinc. According to the first process, copper, cobalt, and nickel are removed from the zinc electrolytes either in a batch process or in a continuously working process in the first stage of the solution purification. The second stage is the removal of cadmium, and the third stage-if required-is utilized as a support stage for the process.

According to the second solution purification process utilizing arsenic as auxiliary agent for zinc, the solution purification takes place in three stages, of which the first and third stage are generally continuous, and the middle stage is an automatic batch process. The main part

of the copper is separated from the zinc electrolytes in the first stage. The rest of the copper is separated together with cobalt, nickel, and germanium in the second stage. Mainly, cadmium is separated in the third stage.

The second stage (the batch process) in a three-stage solution purification process is normally carried out as follows utilizing arsenic as auxiliary agent: Charging of the zinc electrolyte in the reactor is started. If the reactor is half full, for example, mixing is started, and charging with zinc powder can start. Charging of the powder takes place initially quite fast in order to achieve

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a sufficient content in the reactor. Charging is slowed toward the end of the reactor filling process, but is still continued until the overall amount of zinc calculated for the formulation has been added. A co-analysis of the solution is carried out after a predetermined time period, and the formulation is ready if this analysis shows that cobalt has been deposited in a sufficient amount. If the analysis result is insufficient, charging with powder is continued until an adequate cobalt deposition has been achieved. The obtained deposition is not removed after each deposition, but, rather, several depositions are

carried out one after the other, wherein the deposition is removed only from time to time.

Dosing zinc powder has presented a great problem in the past. A "sufficient" powder amount is generally added to achieve a good final result. Even small disruptions normally lead to an increase of the utilization of powder, and the return to the earlier small additions has required great efforts. In other words, there are no suitable indicators for the adequacy of the fed powder.

It has already been known for a long time that the precipitation obeys the following equation:

$$k \times t = \ln \frac{C_0}{C_t},$$

wherein

k = coefficient of deposition rate

t = deposition time

C<sub>0</sub> = initial content

C<sub>t</sub> = content during running time

According to this equation, the deposition takes place when the correct conditions are present in the reactor, when the amount of zinc powder is sufficient, et cetera. However, it has been shown that an increase of the addition of powder beyond the point of "sufficient amount" does not accelerate the deposition. On the other hand, an excessive



use of powder can even slow the reaction, wherein the reason for this is the formation of alkaline zinc sulfate.

In the Finnish patent publication 66 027, a solution purification process for zinc electrolyte is described, in which the amount of zinc powder required for the removal of copper is adjusted in such a way that it corresponds approximately to the stoichiometric amount required for the removal of copper from the solution. The addition of zinc powder can be adjusted with the aid of the redox potential of the electrolyte solution. The redox potential is adjusted in order to control the addition of zinc powder in such a way that the potential of the electrolyte is kept within the range of +200 to -600 mV. The used redox range defines the extent of copper removal and limits the deposition of other metals. The solution, from which copper is removed, is then fed to the removal of cobalt.

In the publication by Sawaguchi et al. entitled "Zinc Electrolyte Purification at Ijima Zinc Refinery," MMIJ/AusIMM Joint Symposium 1983, Sendai, p. 217-229, it is mentioned that the adjustment of a potential was used to adjust the germanium content in order to sufficiently lower the germanium level in the electrolyte solution in the second stage of solution purification. The germanium level

can be kept below 10 ppm if the potential is accordingly adjusted within the range of -610 to -640 mV.

In the aforementioned publication, the measurement of a redox potential is used for the purpose of adjusting the extent of removal of metal removed from the solution. This is, of course, an important factor with regard to the quality of the end product. Another factor that influences the production costs of zinc is the zinc power amount used during solution purification. As became clear from the Finnish publication 66 027, the original amount of added zinc powder roughly corresponds, for example, during the removal of copper, to the stoichiometric amount, whereupon the powder is added according to the requirements of the situation. It also may be the case that the mentioned publication mentions the adjustment of the additions with the aid of the redox potential, but the disclosed range (+200 to -600 mV) reflects, on the other hand, that the mutual dependency between the addition and the potential has remained unclear.

According to the invention, the addition of zinc powder can be adjusted in such a way, in particular during solution purification of zinc electrolyte, that it remains within the optimal range. The essential characteristic

features of the invention become clear from the enclosed claim 1.

In the second stage of solution purification—during so-called cobalt removal—the copper that remains in the solution after copper removal is deposited out of the solution together with cobalt, nickel, and germanium. The following table shows the amounts of elements that occur in the second stage of the applied solution purification. The residual contents of the solution obtained from the second stage must be extremely low:

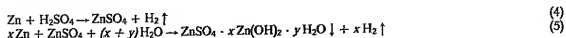
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Element	Original Content	End Content
Cu	50-150 mg/l	< 0.1 mg/l
Co	10-50 mg/l	< 0.2 mg/l
Ni	10-50 mg/l	< 0.1 mg/l
Ge	0.1-3 mg/l	< 0.02 mg/l

As explained above, metallic zinc powder and  $\text{As}_2\text{O}_3$  are utilized during the deposition. The deposition process follows the following reaction equations:



The deposition of germanium is unknown. The dissolution of Zn powder takes place as secondary reaction:



The arsenic amount is easily adjusted according to the initial content. As a consequence, the use of an excessively low or excessively high amount leads to difficulties during the deposition or to a high end content of arsenic.

It was surprisingly shown that optimal deposition conditions can be maintained by utilizing excessive amounts of Zn powder by adjusting the amount of added Zn powder with the aid of the redox potential. The measurement shows at the same time possible disruptions in the addition of powder. The invention will be described in the following with reference to the enclosed drawings, in which the essential features of the invention are graphically illustrated, wherein:

Fig. 1 shows the removal of cobalt from the electrolyte solution with different values of the redox potential as a function of time;

Fig. 2 shows the removal of nickel in the same way as above; and

Fig. 3 shows the removal of germanium in the same way as above.

It becomes clear from the drawing that the maximum deposition of cobalt and nickel is achieved already with the potential -575 mV. The maximum deposition of germanium occurs within the range of -600 to -625 mV. The redox potential was measured with a platinum electrode; the reference electrode used was a calomel electrode.

During the research arranged for this purpose, it was discovered that the amount of Zn powder used can be easily reduced to half of the previously amount used by adjusting the addition of powder with the aid of potential measurements, wherein the degree of contamination remains the same. This means that the production capacity of a system can be considerably increased, wherein the achieved usefulness can be calculated based on the yield when the electrolysis is the limiting factor of the process. The reduction of the production costs in zinc powder alone likewise represents a considerable advantage.

According to the new adjustment process, the addition of Zn powder into the reactor is adjusted to a specific value with the aid of redox potential measurements during the duration of the filling of the reactor during the second stage of the solution purification. The amount of

fed powder is selected in such a way that the  $\text{Cu}^{2+}$  occurring together with the solution in the reactor does not dissolve the cobalt arsenide or nickel arsenide of the deposition already present in the reactor, but copper is deposited. On the other hand, the addition of zinc powder must be such that the Zn powder does not dissolve and that no arsine is formed, even though the solution also contains arsenic. The formation of arsine is hazardous per se due to the environmental danger it represents, but leads of course also to increased consumption of zinc powder. We were able to show that the amount of arsine released together with the exhaust gas is considerably lower than before when the potential adjustment is utilized. This is attributed to the fact that, now, the potential does not reach such a low value that the production of arsine would be possible. It has been shown in practice that a good solution can be obtained in this stage by adjusting the redox potential at the calomel electrode within the range of -480 to -550 mV. When the reactor is full, the copper that remains in the solution after the first stage of solution purification is likewise removed according to the preceding description. The addition of zinc powder is then adjusted in such a way that the deposition of cobalt, nickel, and germanium starts. This potential range at the calomel electrode amounts in

practice to -570 to -650 mV. Each contaminant has its own potential range, wherein the amount of old deposition present in the reactor influences the optimal range.

By using the redox potential measurement, it is thus possible to adjust the addition of zinc powder in such a way that the desired potential is maintained and these metals are deposited, but at the same time, an excessive use of Zn powder is prevented. If the contents regarding the different contaminants in the solution to be fed into the reactor, as well as the amount of deposition present in the reactor according to the preceding formulations, are known, it is possible to experimentally define the deposition rate,

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whereupon the charging with powder is stopped.

The adjustment of the redox potential in the second stage of the solution purification, where the process was operated as a batch process, was described previously. However, the adjustment of the redox potential can also be realized in a continuous process. The removal of cobalt can thus be carried out continuously, or the adjustment of the redox potential can be utilized in other stages of the solution purification.

The invention is explained in the preceding description mainly with reference to a process that utilizes arsenic as auxiliary agent. However, it should be mentioned that the process can also be applied on a process that utilizes other auxiliary agents, wherein this utilization is fully in agreement with the idea of the invention. The optimal values of the redox potential can vary slightly in comparison with the aforementioned data, but not to a considerable extent.

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